

## Environmental status of water and sediment around submarine outfalls – west coast of Portugal \*

### *Qualidade da água e dos sedimentos na zona circundante de oito emissários submarinos – costa oeste de Portugal*

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#### ABSTRACT

The sea along the western coast of Portugal presents hydrodynamic conditions that place it among the most favourable of European coastal waters for dilution and dispersion of waste water. Thus it is an appropriate zone for the location of submarine outfalls. According to the European Union Directives and Portuguese Regulations the waste waters produced by this densely populated coast should be treated, therefore 18 wastewater treatment plants with submarine outfalls were built along the coast.

Between 2002 and 2004, five sampling campaigns were performed in seven outfalls that were selected to participate in water and sediment quality surveys supported by INAG (Portuguese Water Institute), and performed by the Hydrographic Institute of the Portuguese Navy.

The water quality assessment was based on 10 chemical and physical parameters, including heavy metals. The results were compared with reference values and data from the largest flow outfall located at Guia, which has an autonomous monitoring program. In order to evaluate significant differences in water quality between years and sampling sites, statistical analyses were performed.

Sediments were evaluated for grain size, heavy metals, PAH, hydrocarbons, chlorinated pesticides and PCB. In order to evaluate the level of pollution of the different areas where the outfalls are located, the concentration factor (CF) (sediment/water elemental concentration ratio) was calculated and compared with the recommended values for the CF of each element.

The water sampling program did not allow identifying a clear seasonal evolutionary pattern. The environmental status of the waters surrounding the outfalls discharges comply, to a great extent, with the reference values proposed by INAG and did not reveal high levels of contaminants. Due to the low sorptive capacity of the sediment for contaminants, trace metals, hydrocarbons and PAHs have a low environmental impact.

The values of the concentration factors for metals are below the recommended values.

**Keywords:** Portugal, submarine outfall, monitoring, receiving waters, sediments.

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## RESUMO

A costa oeste de Portugal apresenta condições hidrodinâmicas que a colocam entre as zonas mais favoráveis para a diluição e dispersão de águas residuais sendo, por isso, uma região adequada para a localização de emissários submarinos. Dos 18 emissários submarinos construídos ao longo da costa foram seleccionados sete da costa oeste. Cinco campanhas de recolha de amostras foram levadas a cabo entre 2002 e 2004 para participar em pesquisas de qualidade de água e de sedimento suportadas pelo INAG (Instituto da Água) e realizadas pelo Instituto Hidrográfico da Marinha Portuguesa. A avaliação da qualidade das águas baseou-se em parâmetros físicos e químicos, bem como metais pesados. Os resultados foram comparados com valores de referência e com os dados do emissário da Guia que tem um programa de monitorização autónomo. Os sedimentos foram avaliados para parâmetros químicos, metais pesados e granulometria. Para avaliar o nível de poluição das diferentes áreas, o factor de concentração (FC) foi calculado e comparado com os valores recomendados para o FC de cada elemento.

**Palavras-chave:** Portugal, emissário submarino, monitorização, meio receptor, sedimentos.

## 1. INTRODUCTION

Portuguese coastal waters offer hydrodynamic conditions, associated with wind wave action, which are among the most favourable in Europe, for dilution and dispersion of waste water. To take advantage of this fact some municipalities dispose their urban effluents in these coastal waters through submarine outfalls, after different levels of treatment onshore.

The Hydrographic Institute of the Portuguese Navy was asked to develop a quality survey and also to characterize and monitor the main Portuguese estuarine and coastal areas in order to fulfil national obligations regarding International Conventions as well as directive 76/464/EEC for priority substances in the marine environment, Directive 91/676/EEC for nitrates from agriculture sources, Directive 91/271/EEC for urban waste waters and the Water Framework Directive 2000/60/EC. In this paper only the monitoring of the water column and sediments in the adjacent zone to ocean outfalls is reported.

Along the Portuguese coast, eighteen small and medium outfalls were reported in 2006 (Fig.1). Since this study was carried out from 2002 to 2004, some of them had not yet been built. The Portuguese Water Institute (INAG) – which promotes the management and conservation of littoral and estuarine areas and hydrologic resources – selected seven among them to accomplish a water and sediment quality survey, on the Portuguese western coastal waters.

From north to south the selected ocean outfalls were: Viana do Castelo (Viana), Matosinhos (Mat), Gaia (Gaia), Espinho (Esp), Leirosa (Leirosa), Sesimbra (Ses) and Sines (Sines), (Figure 1).

Water column results were compared with INAG reference values and with data from the largest flow outfall located at Guia (Guia), which has an autonomous monitoring program whose sampling and analytical tasks are carried out by LNEG.

The aim of this study is to present water column spatial and temporal distributions and compare results with reference values, and characterize sediments in the vicinity of some Portuguese submarine outfalls from 2002 to 2004.

## 2. OUTFALL CHARACTERISTICS

In Table 1 outfall characteristics are presented as well as the type of treatment performed at the waste water treatment plant (WWTP) up to the discharge. Four kinds of treatment can be found at the eight WWTP: a preliminary one, two primary, five secondary and one tertiary. Exploration daily flow varied from 2500 to 150 000 m<sup>3</sup>/day (Fig.2). Despite the similar lengths among the outfalls (with the exception of Sesimbra), the depth of the disposal waters range from 9 meters to 45 meters. The population equivalent served is also quite different, varying from 15 000 to 750 000 (Fig.2). Leirosa is mainly an industrial outfall that serves a paper and a pulp mill, each with a different kind of treatment, one primary and other secondary.

The high level of treatment performed at Sesimbra (UV disinfection) is justified by the neighbourhood of sandy beaches highly populated during summertime.

## 3. METHODOLOGY

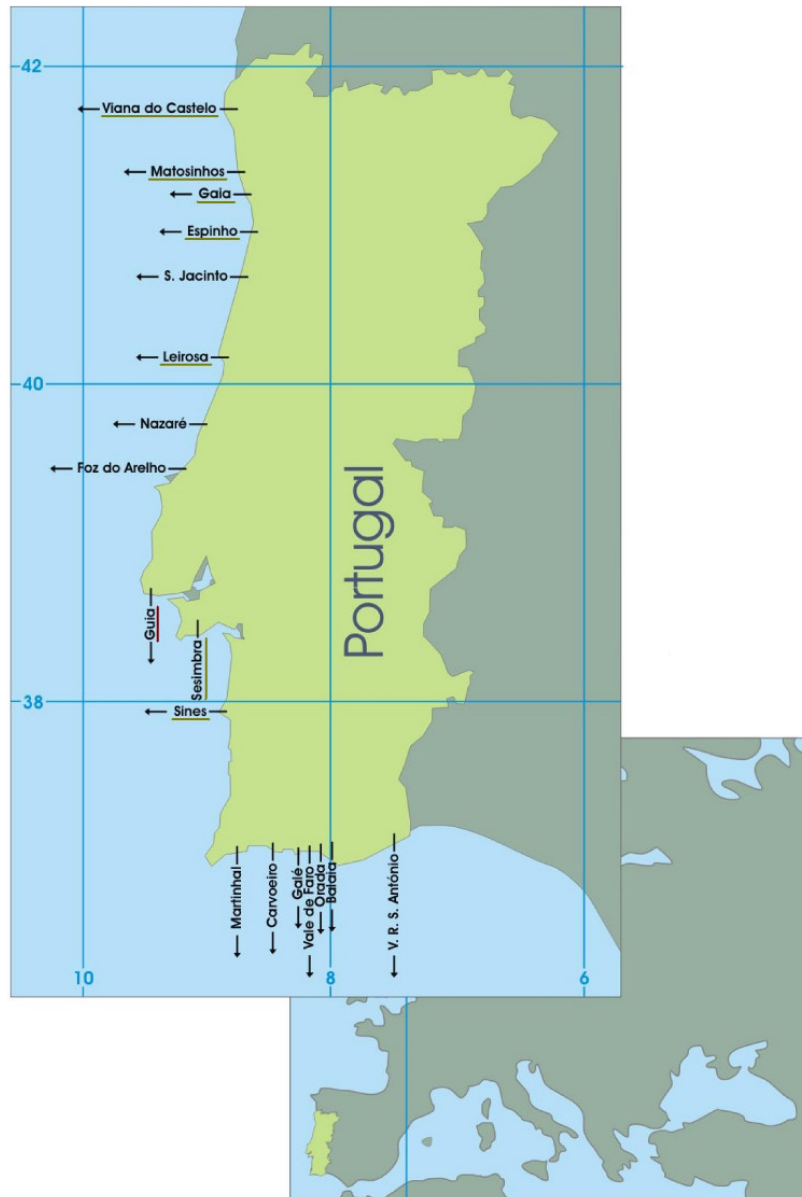
This study was performed from 2002 to 2004, twice a year during spring and autumn (in 2004 sampling was carried out only in autumn). Surface and bottom samples were taken at three sampling stations around each outfall port (except for Sesimbra that had seven sampling stations) according to predicted dispersion through local current patterns.

### 3.1 Water sampling

Surface and bottom waters were collected using *Niskin* bottles.

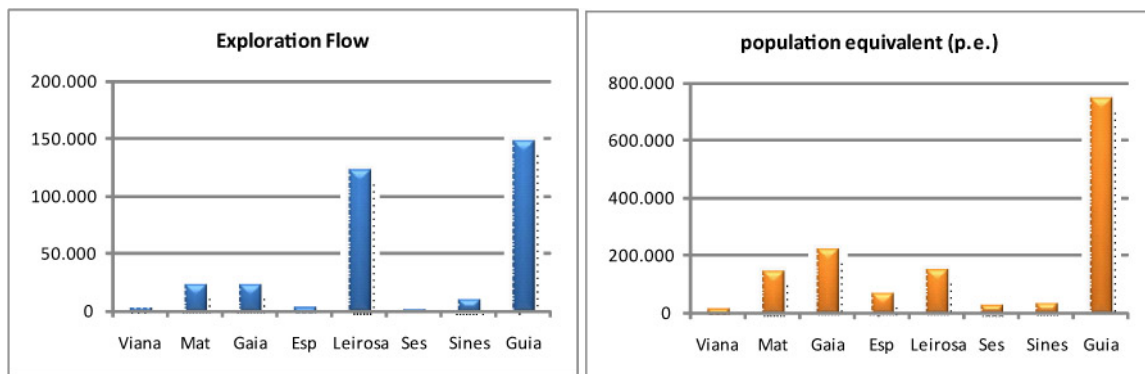
Water samples were analyzed for pH, salinity, dissolved oxygen, chlorophyll *a*, nutrients and trace metals.

Samples for salinity, nutrient and trace metals analysis were filtered after sampling with a nitrogen pressure system and polycarbonate filters with 0,4 µm porosity. Samples for Chlorophyll *a* analysis were filtered in a vacuum system with Gelman GN-6 filters with 0,45 µm porosity. Water samples for trace metal analysis were preserved with nitric acid. Water samples for nutrient analysis were frozen to -20 °C. Water temperature measurements were made *in situ*.



**Figure 1.** Submarine outfalls of the Portuguese coast. (Adapted from Reis & Neves, 2001).

**Figura 1.** Emissários submarinos da costa portuguesa (adaptado de Reis & Neves, 2001).



**Figure 2.** Submarine outfalls of the Portuguese coast – exploration flow and population equivalent (Adapted from Reis & Neves, 2001).

**Figura 2.** Emissários submarinos da costa portuguesa – caudal de exploração e população equivalente (adaptado de Reis & Neves, 2001).

**Table 1.** Characteristics of the 8 outfalls Source: Freire (2006) and LNEC (2003)**Tabela 1.** Características dos 8 emissários submarinos Fonte: Freire (2006) e LNEC (2003).

Characteristics	Submarine Outfalls							
	Viana do Castelo (Viana)	Matosinhos (Mat)	Gaia (Gaia)	Espinho (Esp)	Leirosa (Leirosa)	Sesimbra (Ses)	Sines (Sines)	Guia (Guia)
Date of entry in service	1973	1999	1992	1999	1995	2000	1978	1994
Exploration Flow (m <sup>3</sup> /day)	3 000	25 000	24 260	5 035	100 000-150 000	2 700	11 535	150 000
Project Flow (m <sup>3</sup> /day)	77 760	82 339	?	101 520	172 800	6 000	172 800	450 000
Treatment Type (WWTP up to the discharge)	Secondary	Primary	Secondary	Secondary	Primary Secondary	Tertiary	Secondary	Preliminary
Outfall Length (m)	2 250	2 748	2 192	2 000	1 163 (onshore) + 1 526 (offshore)	500	2 432	2 750
Outfall Diameter (mm)	900	1 600/1200	800	800/630/400	1 200	500	1 100	1 200
Maximum Depth (m) (HZ)	-17,5	- 27,0	- 30,0	-9,0	-11,0	-20	-38,0	-45,0
Population equivalent (p.e.)	20000 (urban) (industrial)	150 000	230 000	74 000	Industrial (paper pulp and landfill) and urban 155 000	30 000	Industrial (chemistry and refinery) and 38 000 (urban)	753 397
Outfall Material	Reinforced concrete (with steel)	Concrete (onshore) /HDPE (offshore)	HDPE	HDPE	GRP (onshore) and MDPE (offshore)	HDPE	Reinforced concrete (with steel)	HDPE
Diffusors Type	Reinforced concrete with steel, 100 m, Ø 600 mm, 15 holes with 140 mm	HDPE, 320 m, Ø [450-1200 mm], 76 wastewater diffusion pipes	Single outlet Ø 800 mm	HDPE, 105 m, Ø [400-800 mm], 70 wastewater diffusion pipes	MDPE, 313 m, Ø 1200 mm, 85 holes Ø 100 mm, 30 of them with Red Valve type	Single outlet with "horse neck" discharge through rubber duck-bill check valve	Reinforced concrete, 240 m, Ø 1200 mm, 60 holes with 125 mm and final hole with Ø 200 mm	Two HDPE branches with 1800m. The last 400m with 80 holes Ø 100 mm every 5m

WWTP – Waste Water Treatment Plant; HZ – Hydrographic Zero; HDPE – High Density Polyethylene; MDPE – Medium Density Polyethylene; GRP Glass-reinforced plastic

### 3.2 Water analyses

pH determination was carried out using specific pH devices that were calibrated prior to the analysis with known pH solutions. Salinity determination was based on sample electric conductivity measurements with an electrode salinometer calibrated with standard ocean water (APHA *et al.*, 1998). Dissolved oxygen determination was based on an iodometric method (APHA *et al.*, 1998). Chlorophyll *a* determination was based on sample filtration and filter residue extraction with acetone followed by UV-Vis spectroscopy determination (APHA *et al.*, 1998). The automated determination of nitrate, nitrite, ammonium and phosphate was done in a Skalar San<sup>plus</sup> Segmented Flow Analyzer. Nitrate determination was based on the cadmium reduction method as the sample flows through a column containing granulated copper-cadmium to reduce the nitrate to nitrite. The procedure was the same for nitrite, preventing the sample from passing through the cadmium column (APHA *et al.*, 1998; IOS, 1996). Ammonium determination was based on the modified Berthelot reaction where ammonium is oxidized to a green complex (APHA *et al.*, 1998; Krom, 1980). Phosphate determination was based on an antimony-phospho-molybdate complex followed by reduction to an intensely blue-coloured complex (APHA *et al.*, 1998; Boltz & Mellon, 1948). Trace metals were liquid-liquid extracted and analyzed by atomic absorption spectrometry (Magnusson & Westerlund, 1980).

The Guia autonomous sampling program follows a similar methodology except for trace metals. Instead of AAS, Guia metals and other elements were analysed by the TXRF (Total-reflection X-Ray Fluorescence) multielement technique, preceded by chemical separation of the salt matrix and preconcentration of the metallic elements as dithiocarbamates using APDC (Costa *et al.*, 1999).

### 3.3 Water data Analysis

Average values were calculated for each outfall and reported in 4 charts for surface waters. To evaluate differences among sampling stations (spatial analysis) and among sampling dates (temporal analysis), analyses of variance were performed using STATISTICA software StatSoft<sup>®</sup>, with a 0,05 significance level. Correlation analyses were also made between some physical and chemical parameters. A T test was performed in order to compare Guia results with those from the other outfalls.

### 3.4 Sediment Sampling

Surface sediment samples were collected using a stainless-steel grab. After homogenization, samples for chemical analysis were wet sieved to 2 mm and stored frozen in pre-cleaned glass jars until analysis. For granulometric and total organic carbon analysis no preservation was required.

### 3.5 Sediment Analysis

Sediment samples were analyzed for trace metals, organochlorine pesticides, PCBs, hydrocarbons, polyaromatic hydrocarbons (PAHs), grain size and total organic carbon (TOC). Trace metals and organochlorine compounds were analyzed on freeze-dried sediments while wet samples were analyzed for hydrocarbons and PAHs contents. Samples were totally digested with strong acids and analyzed by atomic absorption spectrometry

for metal analysis (Loring, 1990). Organochlorine pesticides and PCBs were soxhlet extracted followed by an alumina clean-up, silica fractionation and determination with GC-ECD and capillary column (Smedes & Boer, 1997). Hydrocarbons and PAHs were extracted by saponification (NaOH) followed by a liquid-liquid extraction with pentane and a silica-gel clean-up. Hydrocarbons and PAHs were determined using UVF and GC-MS, respectively (Kelly *et al.*, 2000).

Superficial sediments grain-size was analyzed by laser forward-scattering, in the MALVERN 2000 equipment. Classical sieving methods were used for grain sizes higher than 500 µm. Sediments from Guia were wet sieved in order to obtain the silt clay fraction (< 63 µm), which was dried and submitted to microwave acid digestion prior to TXRF analysis (Costa *et al.*, 1999).

### 3.6 Sediment data analysis

Sediment data analysis considered the five sampling campaigns performed on February and September 2003, March and September 2003 and September 2004. Arithmetic averages for the fine fraction, metals, hydrocarbons and PAHs were considered for each sampling campaign taking into account the number of sampling sites in each outfall area: seven for Sesimbra outfall and three for the other ones.

## 4. RESULTS AND DISCUSSION

### 4.1 Water

In order to comply with Directive 91/271/EEC, INAG developed a document (INAG, 1998) that set limits for the receiving waters near outfall discharges, based on their location in sensitive or less sensitive zones. This document establishes four parameters and their summertime and wintertime thresholds with the objective to control eutrophication occurrence in less sensitive waters – transparency, percent saturation of dissolved oxygen (DO), dissolved nitrate and chlorophyll *a*. These parameters were compared with the guidelines identified on Table 2.

February field work was considered as wintertime sampling campaign and September field work was considered as summertime sampling campaigns, according to the INAG guidelines.

The percent saturation of DO, on the five months study, comply with Directive 76/160/EEC and with INAG guidelines that states that 90% of the results should surpass 90% of saturation, in summertime, which reveals good oxygen concentration levels in these coastal waters (Fig.3).

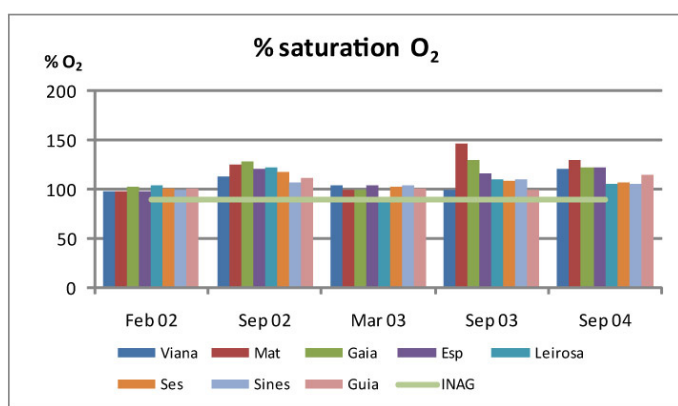
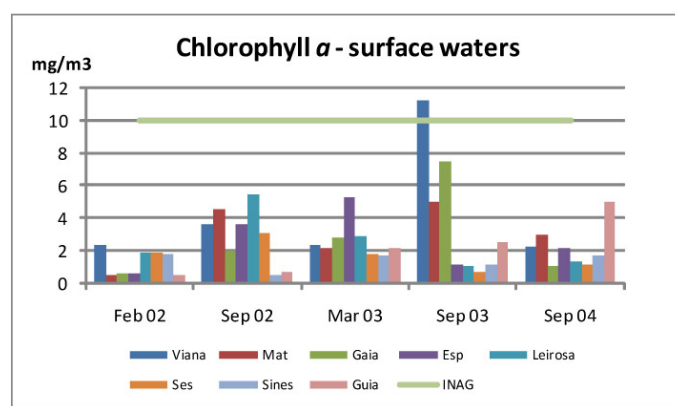
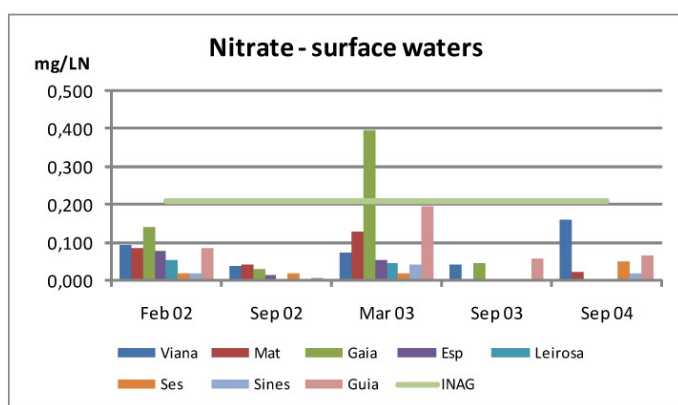
Nitrate in surface waters behave in a similar way among sampling sites. Throughout the five months, Gaia station surpasses INAG guideline with a concentration of 0,4 mg/L N in March 2003 (Fig.4).

The sampling season can influence the presence of nitrate in surface waters, which can be associated to the precipitation and runoff in the early months of the year (February, March) or even to the natural biogeochemical cycles. Nitrate is the main nutrient of phytoplankton, here represented by chlorophyll *a*. Even though no significant correlation was found, in September 2003 a peak of 11,2 mg/m<sup>3</sup> chlorophyll *a* was observed in surface waters that surpass the INAG guidelines at Viana do Castelo (Fig. 5), and at the same time a nitrate depletion was observed, as showed in Figure 4.



**Table 2.** Reference values for surface waters, from Directive 76/160/EEC and INAG**Tabela 2.** Valores de referência para águas superficiais da Directiva 76/160/EEC e do documento INAG.

Parameter	Bathing Waters Directive		INAG Guidelines (less sensitive zones)
	76/160/EEC		
	Guide value	Mandatory value	
pH		6-9	
Transparency		2	>2 m, in wintertime
(Dissolved Oxygen) % Saturation of DO	80-120		>90%, in summertime
Dissolved Nitrate			<0.210 mg/L N, wintertime
Chlorophyll <i>a</i>			<10 mg/m <sup>3</sup> , in summertime

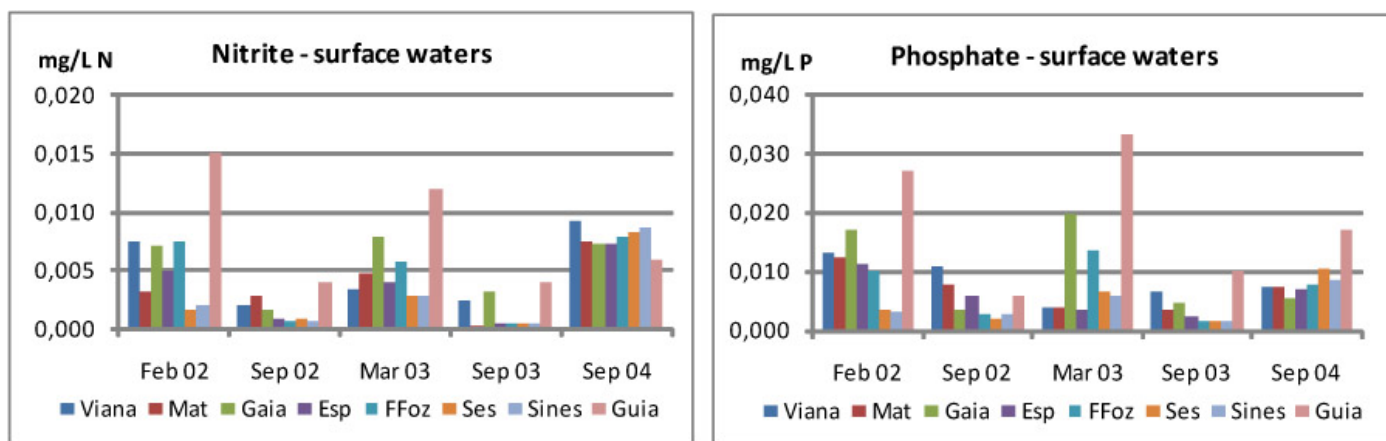
**Figure 3.** Percent saturation of dissolved oxygen in surface waters and INAG guideline (90%).**Figura 3.** Percentagem de saturação nas águas de superfície e valor INAG (90%).**Figure 5.** Chlorophyll *a* concentration (mg/m<sup>3</sup>) in surface waters and INAG guideline (10 mg/m<sup>3</sup>).**Figura 5.** Concentração em clorofila *a* (mg/m<sup>3</sup>) nas águas de superfície e valor INAG (10 mg/m<sup>3</sup>).**Figure 4.** Nitrate concentration (mg/L N) in surface waters and INAG guideline (0,210 mg/L N).**Figura 4.** Concentração em nitrato (mg/L N) nas águas de superfície e valor INAG (0,210 mg/L N).

Confirming the buffer capacity of sea water, pH presented values in the range of 8-8,2 in all studied coastal waters, complying with Directive 76/160/EEC.

Other parameters like nitrite and phosphate were also evaluated in this study and present an evolutionary curve similar to nitrate. At Guia, the highest urban flow outfall, an elevated incidence of those parameters was found in surface waters (Fig.6).

Coastal waters usually have low concentrations in ammonium and in most cases its presence is associated with the urban wastewater disposal through the outfall (Santos et al. 2002). As in this study no faecal survey was done we can only presume that the presence of this contaminant, even in low concentration (from 0 to 0,115 mg/L NH<sub>4</sub>), can be associated with the outfall plume.

Surface waters showed significant monthly differences ( $p < 0,05$ ) for temperature, % saturation, nitrate and nitrite. The sampling strategy that covered two seasons per year (spring and autumn) can be responsible for the observed differences. In fact, the local weather in February and September is quite different in Portugal and may affect in a significant way the difference of water temperature. Furthermore, in temperate



**Figure 6.** Nitrite (mg/L N) and phosphate (mg/L P) concentration in surface waters.

**Figura 6.** Concentração em nitrito (mg/L N) e fosfato (mg/L P) nas águas de superfície.

coastal waters nitrate concentration in surface water reaches a maximum in winter when photosynthesis is minimal and the mixture of water by convection is predominant. In summer the nitrate is consumed by phytoplankton and its concentration in surface water decreases (Tait & Dipper, 1998). These field results follow this general trend.

Among sampling stations dissolved oxygen and phosphate showed significant differences ( $p < 0,05$ ). ANOVA performed without Guia results showed no significant differences for phosphate, which means that the receiving waters around Guia outfall may be responsible for this difference.

Chlorophyll a at surface waters did not show any significant differences among sites or months. A similar result was obtained for ammonium.

Bottom water results did not present any evolutionary trend among sites and among months, which rule out any interpretation. Nevertheless, ANOVA results were reported and significant monthly variations ( $p < 0,05$ ) for temperature, dissolved oxygen, salinity and ammonium were found. Due to the wastewater disposal at the bottom waters these parameters can behave in different ways if water stratification exists or not, depending on the weather conditions.

Among sampling stations salinity, nitrate, phosphate and ammonium presented significant differences ( $p < 0,05$ ), which can be related to the different characteristics to the outfall plume: flow, urban or industrial waste water.

In order to evaluate the differences between Guia and the other seven outfalls a t test was applied to the five month period. Guia surface waters were different from Espinho, Sesimbra and Sines, only for phosphate concentration but at a slighter amount.

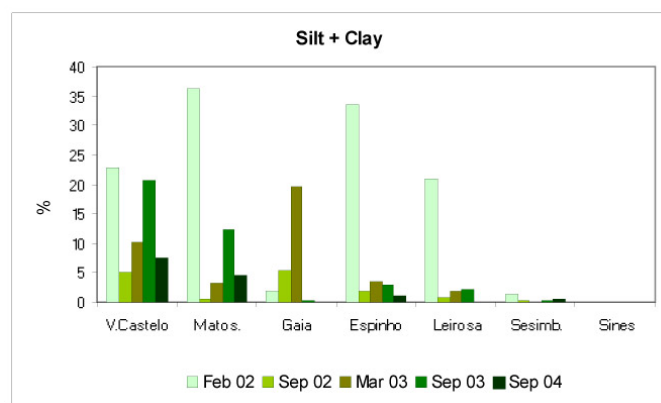
Guia bottom waters present rather different results and consider other parameters: water temperature is only different from Sesimbra and salinity is only different from Viana. In what concerns dissolved oxygen, % saturation, nitrate and phosphate Guia bottom waters are different from Leirosa, Sesimbra and Sines.

#### 4.2 Sediments

In contamination studies sediment monitoring plays an important role because sediment acts as a sink where

contaminants can be stored and as a source of these contaminants to the overlying water and to biota (Baudo et al., 1990; Loring, 1991). In low energy environments the fine grain sediments deposited have a high sorptive capacity (Kersten & Smedes, 2002). In contrary, when the energy of the overlying flow is high, like some coastal and oceanic areas, the sorptive capacity of the sediment for contaminants is small with consequent low depositional rates. Surrounding areas near the studied ocean outfalls are usually very hydrodynamic. Superficial sediments samples are therefore sandy and low in total organic carbon. This almost complete lack of sediment fine fraction limits the affinity and adsorptive capacity for contaminants and thus, reduces the environmental impact of these outfall discharges.

Figure 7 shows that the average sediment fine fraction ( $<63 \mu\text{m}$ ) for each outfall area in the studied period was low with occasional slight rises. Therefore, trace metal contents, PAHs, organochlorine pesticides and PCBs were low, usually at limit of quantification levels. This confirms the low sorptive capacity of these sediments. Besides, the unknown contaminant concentration in outfall discharges disables any prevision about higher contaminant concentrations in water column and superficial sediments.



**Figure 7.** Average superficial sediment fine fraction ( $<63 \mu\text{m}$ ) for the Portuguese ocean outfall areas.

**Figura 7.** Fração fina dos sedimentos superficiais ( $<63 \mu\text{m}$ ) na zona de descarga dos emissários submarinos.

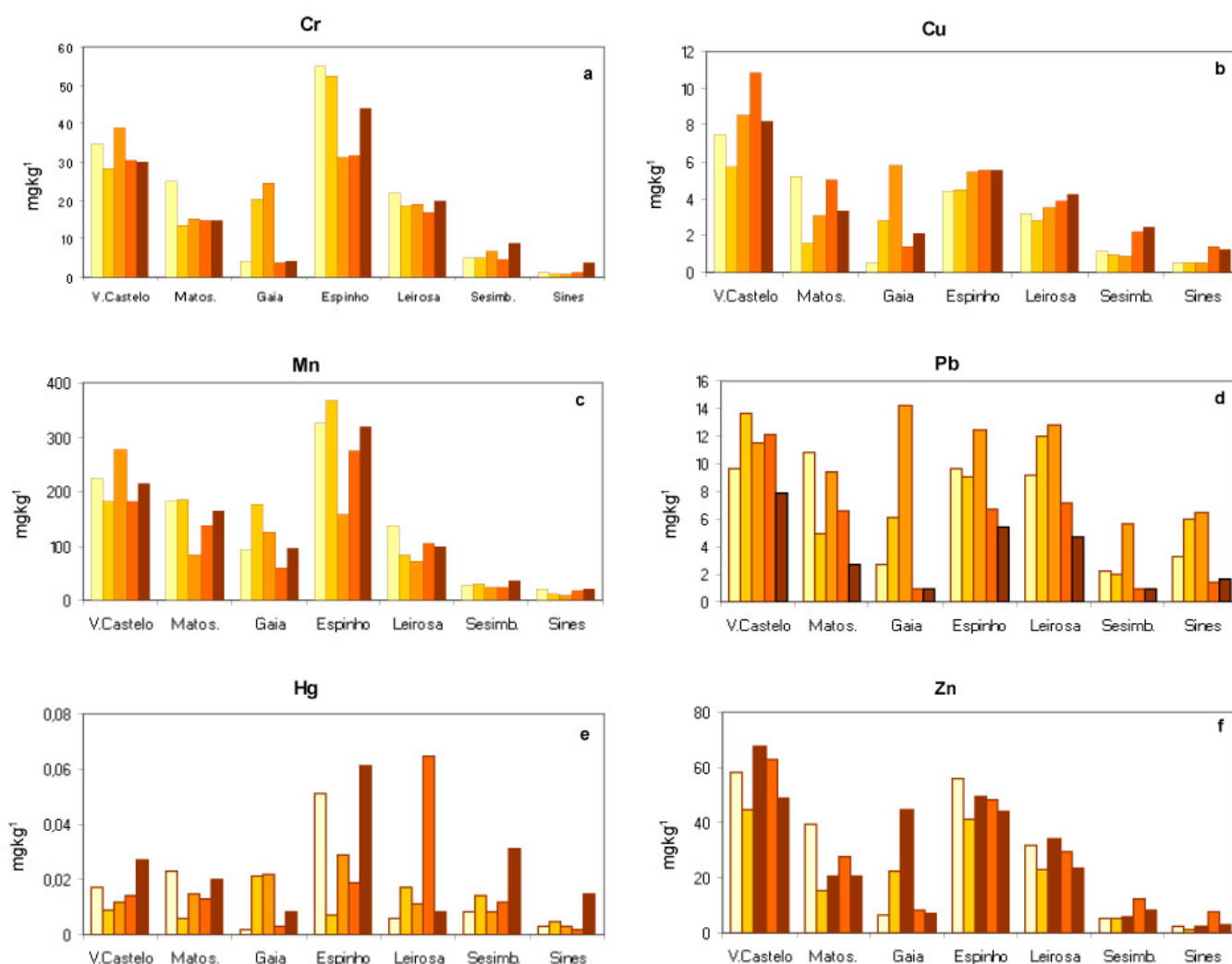
In Figure 8 the average content of trace metals in superficial sediments from each outfall area is considered. Despite the many existing variations, a general trend for a metal increase where the fine fraction was slightly superior was observed. In fact, temporal patterns in Figure 7 and Figure 8 have some similarities which suggest that the fine fraction, though not significant, interfered somewhat in contaminant behaviour. Manganese showed significant concentrations in Viana do Castelo and Espinho outfalls which can be related with natural constitution of sediments (Figure 2-c) (Araújo *et al.*, 2002).

Natural and anthropogenic polyaromatic hydrocarbons (PAHs) are common in the marine environment. Even remote areas have small PAHs concentrations from atmospheric inputs. Coastal areas are affected from multiple sources associated with human activities (Page *et al.*, 1999). Figure 9 shows average total PAH concentrations in sediments near the ocean outfall areas. Matosinhos and Viana do Castelo outfalls registered increased concentrations that can be related to the correspondent increase in the sediment fine fraction. Conversely, the Sesimbra outfall area was characterized by

higher levels in PAHs even if no significant sediment fine fraction was detected (Figure 7 and Figure 9).

Figure 10 shows that the temporal average concentrations of hydrocarbons in superficial sediments near the outfalls have a similar behaviour as the PAHs (Figure 9). In fact, again Matosinhos, Viana do Castelo and Sesimbra outfalls show higher concentrations, which can be related to the fine sediment fraction variability as well as with some occasional and isolated conditions.

Perilen is a biogenic PAH as it can be generated through biological processes. However, it can not be used as a single criterion because it can be also produced during combustion processes (Wang *et al.*, 1999). Another way to assess the contamination source of PAHs is through the quotient of particular aromatic hydrocarbons. Phenanthrene and anthracene concentration rates (P/A) and fluoranthene and pyrene rates (Fl/Py) can be used to characterize contamination sources. When the P/A rate is smaller than 10 and the Fl/Py is greater than 1, PAHs contamination may have its origin in combustion processes (Benlahcen *et al.*, 1997). In Figure 11 the observed cloud of points does not give any certainty about the

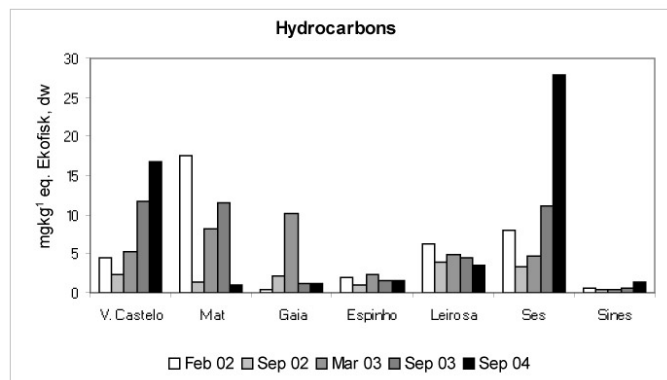


**Figure 8.** Average trace metal concentrations for superficial sediments from the Portuguese ocean outfall areas.

**Figura 8.** Concentração média de metais nos sedimentos superficiais na zona de descarga dos emissários.

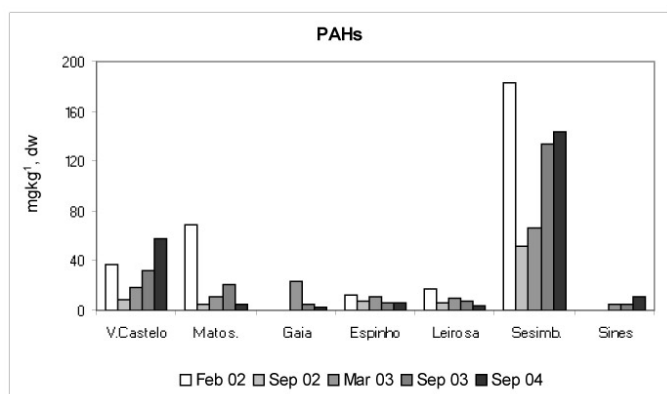


PAHs origin. However, the distribution pattern for Sesimbra outfall (Ses) with corresponding FI/Py rates bigger than 1 suggest that according to the authors, that the PAHs could be formed in combustion processes.



**Figure 9.** Average PAHs concentrations for superficial sediments from the Portuguese ocean outfall areas.

**Figura 9.** Concentração média de PAH nos sedimentos superficiais na zona de descarga dos emissários.



**Figure 10.** Average hydrocarbons concentrations for superficial sediments from the Portuguese ocean outfall areas.

**Figura 10.** Concentração média de hidrocarbonetos nos sedimentos superficiais na zona de descarga dos emissários.

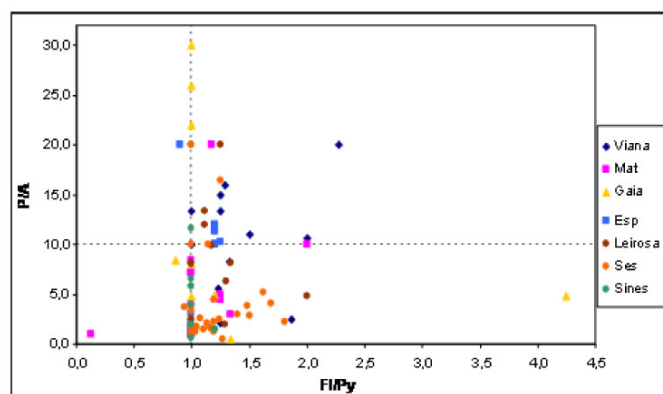
#### 4.3 Concentration factors

Information on the trace metal concentration of sediments and waters is important to evaluate the pollution level of a particular coastal zone. The distribution of trace metals in the sediments is a common procedure to assess the impact of anthropogenic inputs. The metal concentrations in the water column are due to resuspension of bottom sediment, to effluent discharges and to geochemical processes. The concentration factor (CF), sediment/water elemental concentration ratio, accounts for the elemental sediment/water exchanges and reflects the fraction of the element permanently available to benthic communities. In

the present work coastal sediment concentration factors were calculated in order to deduce the level of pollution of the different areas where outfalls are located. Besides the above presented sediment data, Guia monitoring program also included a sediment campaign in autumn 2002. Thus data sets obtained for all sampling sites were calculated in order to compare the obtained concentration factors (OCF) with the recommended concentration factors (RCF) (Costa et al., 1999; IAEA, 1985).

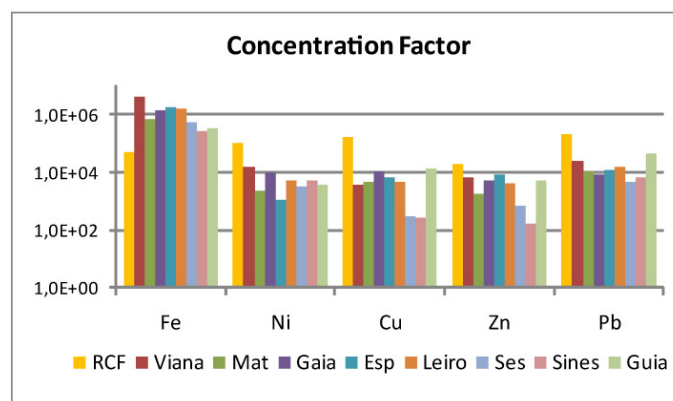
Figure 12 presents this comparison for the eight submarine outfalls, concerning iron (Fe), nickel (Ni), copper (Cu), zinc (Zn) and lead (Pb).

Comparing the obtained CF with the recommended values of each element we can assume that these areas do not show a high level of pollution, since all the elements present OCF below RCF except iron, which does not represent an environmental problem.



**Figure 11.** Phenanthrene and anthracene concentration rates (P/A) and fluoranthene and pyrene rates (FI/Py) for all sampling sites in 2002-2004.

**Figura 11.** Relação entre a concentração de fenantreno e antraceno (F/A) e de fluoranteno e pireno (FI/P) em todos os locais amostrados, de 2002-2004.



**Figure 12.** Concentration factors for Fe, Ni, Cu Zn and Pb obtained in the eight submarine outfalls (autumn 2002).

**Figura 12.** Factores de concentração para Fe, Ni, Cu, Zn e Pb obtidos nos oito emissários submarinos (Outono de 2002).

#### 4. CONCLUSIONS

The design of this water sampling program did not make it possible to establish a seasonal evolutionary pattern of the analysed data. Instead it only gave a "picture" of the environmental state of the waters that surround the eight outfalls, located in less sensitive zones, which comply, to a great extent, with the reference values proposed by INAG, in the five monthly surveys.

In long term surveys variance analysis applied to some physical and chemical parameters usually shows significant differences among sampling months but not among sampling sites pointing out time as the main variability source of the system (Santos & Catarino, 2003; Santos et al., 2006). In this survey, due to the small amount of data, analyses of variance did not exhibit this trend, with the exception of temperature and phosphate and, to a lesser extent, salinity and ammonium.

Comparing Guia results with those of the other outfalls the main differences were found in bottom waters which can be related to the wastewater treatment performed up to the discharge at the WWTP which varied from a preliminary one (at Guia), a primary one at Matosinhos and Leirosa, a secondary one at Viana do Castelo, Gaia, Espinho, Leirosa and Sines and a tertiary one at Sesimbra.

Despite the differences among the outfalls flows, the population equivalent and the waste water treatment at the WWTP, the receiving waters did not present high levels of contaminants.

The lack of randomness and spatial-temporal replication in the sampling strategy limited the representativeness of the data obtained for sediments. Although some individual increases in trace metals, hydrocarbons and PAHs could not be explained due to little data information, the most frequent low concentrations showed the low sorptive capacity of the sediment for contaminants. Sediments were sandy and poor in total organic carbon, characteristics of hydrodynamic areas that correspond to the location of the outfalls studied.

No remarkable contamination values were found in the sediments as expressed by the low metal concentrations and the values of the concentration factors, below the recommended values, with exception of iron, where the values found may be due to natural concentrations.

For a better understanding of the results obtained, this kind of surveys should be complemented with the analytical control of the effluent at the WWTP, also useful to test the performance of the waste water treatment at each plant. To cross the waste water characteristics, sometimes with a strong industrial component, with the results of the receiving waters, for the same analytical period, would fulfil one of the objectives of the Water Framework Directive. This kind of approach would provide a better comprehension on the environmental impact and performance of these infrastructures and allow improving, in the future, the design of the environmental monitoring programs.

#### RECOMMENDATIONS

The design of a monitoring program to survey submarine outfalls should take in account microbiological parameters once most of these outfalls disposal are located near sandy

beaches very populated in summertime and even all the year by surfers. Moreover it is also recommended to survey nitrate and chlorophyll concentrations and dynamics to evaluate the possibility of an occurrence of eutrophication.

#### REFERENCES

- APHA, AWWA, WEF (eds.) (1998) - Standard Methods for the Determination of Water and Wastewater, 20th edition.
- Araújo, M. F.; Jouanneau, J.-M.; Valério, P.; Barbosa, T.; Gouveia, A.; Weber, O.; Oliveira, A.; Rodrigues, A.; Dias, J. M. A. (2002) - Geochemical Tracers of Northern Portuguese Estuarine Sediments on the Shelf. *Progress in Oceanography*, 52(2-4):277-297. DOI:10.1016/S0079-6611(02)00011-3.
- Baudo, R.; Giesy, J.P. & Muntau, H. (eds.). (1990) - Sediments: Chemistry and Toxicity of In-Place Pollutants. 1st ed.. 424 p. CRC Press, Florida, USA. (ISBN: 978-0873712521)
- Benlahcen, K.T.; Chaoui, A.; Budzinski, H.; BellocQ, J.; Garrigues, P.H. (1997) - Distribution and Sources of Polycyclic Aromatic Hydrocarbons in Some Mediterranean Coastal Sediments. *Marine Pollution Bulletin*, 34(5):298-305. DOI:10.1016/S0025-326X(96)00098-7
- Boltz, D.F.; Mellon, M.G. (1948) - Spectrophotometric determination of phosphate as molybdophosphoric acid. *Analytical Chemistry*, 20(8):749-751. DOI:10.1021/ac60020a021.
- Costa, M.M.; Barreiros, M.A.; Carvalho, M.L.; Queralt, I. (1999) - Multi-element characterization of estuarine sediments and waters. *X-Ray Spectrometry*, 28(5):410-413. DOI:10.1002/(SICI)1097-4539(199909/10)28:5<410::AID-XRS377>3.0.CO;2-3
- INAG (1998) - Linhas de Orientação Metodológica para a Elaboração dos Estudos Técnicos necessários para cumprir o art.7º, do DL 152/97 - Descargas em zonas menos sensíveis. INAG - Ministério do Ambiente. Lisboa, 1998. (Não publicado).
- EC (2000) - Directive 2000/60/EC, of the European Parliament and of the Council, of 23 October 2000, establishing a framework for Community action in the field of water policy. *Official Journal of the European Communities*, L327:1-73. <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2000:327:0001:0072:EN:PDF>
- EEC (1976a) - Council Directive 76/464/EEC, of 4 May 1976, on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community. *Official Journal L* 129, 18.5.1976, pp. 23-29. <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:31976L0464:EN:HTML>
- EEC (1976b) - Council Directive 76/160/EEC, of 8 December 1975, concerning the quality of bathing water. *Official Journal L* 31, 5.2.1976, pp. 1-7. <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:31976L0160:EN:HTML>
- EEC (1991a) - Council Directive 91/271/EEC, of 21 May 1991 concerning urban waste-water treatment. *Official*

- Journal L 135, 30.5.1991, pp. 40–52. <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:1991:135:0040:045:EN:HTML>
- EEC (1991b) - Council Directive 91/676/EEC, of 12 December 1991, concerning the protection of waters against pollution caused by nitrates from agricultural sources. Official Journal L 375, 31.12.1991, pp. 1–8. <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:31991L0676:EN:HTML>
- Freire, A. (2006) – Campanha de Inspeções a ETAR com Descarga em Zonas Balneares Costeiras 2005. Relatório Técnico, 49p., Inspeção-Geral do Ambiente e do Ordenamento do Território, Lisboa, Portugal. (Não publicado)
- IAEA (1985) – Sediment Kds and concentration factors for radionuclides in the marine environment. Technical Reports Series, N° 247, 73p., International Atomic Energy Agency, Vienna, Austria. ISBN: 9201250851 <http://www-pub.iaea.org/mtcd/publications/PubDetails.asp?pubId=1349>
- IOS – International Organization for Standardization (1996) - ISO 13395:1996 - Water quality -- Determination of nitrite nitrogen and nitrate nitrogen and the sum of both by flow analysis (CFA and FIA) and spectrometric detection, 18 pp., 1996, International Organisation for Standardization, Geneva, Switzerland
- Kelly, C.A.; Law, R.J.; Emerson, H.S. (2000) – Methods for Analyzing for Hydrocarbons and Polycyclic Aromatic Hydrocarbons (PAH) in Marine Samples. Aquatic Environment Protection: Analytical Methods, N° 12, 18 pp., Centre for Environment Fisheries and Aquaculture Science, CEFAS, Lowestoft, UK. Disponível em <http://www.cefas.co.uk/publications/aquatic/aepam12.pdf>
- Kersten, M.; Smedes, F. (2002) – Normalization procedures for sediment contaminants in spatial and temporal trend monitoring. Journal of Environmental Monitoring. 4(1):109-115. DOI:10.1039/B108102K.
- Krom, M. (1980) – Spectrophotometric determination of ammonium: a study of modified Berthelot reaction using salicylate and dichloroisocyanurate. The Analyst, 105:305-316. DOI:10.1039/AN9800500305.
- Loring, D.H. (1990). Lithium — A new approach for the granulometric normalization of trace metal data. Marine Chemistry. 29 (2-3):155-168. DOI:10.1016/0304-4203(90)90011-Z
- Loring, D.H. (1991) – Normalization of heavy-metal data from estuarine and coastal sediments. ICES Journal of Marine Science. 48(1):101-115. DOI:10.1093/icesjms/48.1.101
- Magnusson, B.; Westerlund, S. (1980) - The determination of Cd, Cu, Fe, Ni, Pb and Zn in Baltic Sea water. Marine Chemistry. 8(3):231-244. DOI:10.1016/0304-4203(80)90012-2.
- Page, D.S.; Boehm, P.D.; Douglas, G.S.; Bence, A.E.; Burns, W.A.; Mankiewicz, P.J. (1999) – Pyrogenic Polycyclic Aromatic Hydrocarbons in Sediments Record Past Human Activity: A case Study in Prince William Sound, Alaska. Marine Pollution Bulletin, 38(4):247-260. DOI:10.1016/S0025-326X(98)00142-8
- Reis, M.T.; Neves, M.G. (2001) – Comportamento estrutural de emissários submarinos. Abordagem metodológica, Relatório 24/03-NPE, Proc. 603/14/14053, 171p., LNEC, Lisboa, Portugal.
- Santos, C.; Catarino, J. (2003) – Monitorização Ambiental do exutor submarino de S. Jacinto Caracterização do meio receptor. Relatório INETI, 167p., Lisboa, Portugal. (Não Publicado)
- Santos, C.; Catarino, J.; Marques, E.; Figueiredo, Z.; Trancoso, A.; Marecos, H.; Neves, R. (2002) – Monitoring sea water around the disposal area of Guia submarine outfall. Proceedings of the 2nd International Conference on Marine Waste Water Discharges – Environmental Monitoring, p 1-12. 16-20 September 2002, Istambul, Turquia.
- Santos, C.; Martins, C.; Catarino, J. (2006) - Monitorização Ambiental do Emissário Submarino da Guia. Caracterização do meio receptor – 2005. Relatório INETI, 41p + anexos, Lisboa, Portugal. (Não publicado).
- Smedes, F.; Boer, J. (1997) – Determination of chlorobiphenyls in sediments-analytical methods. TrAC - Trends in analytical chemistry. Vol. 16(9):503-517. DOI:10.1016/S0165-9936(97)00080-0
- Tait, R.V.; Dipper, F.A. (1998) – Elements of Marine Ecology. 462p., Butterworth-Heinemann, Oxford, UK. ISBN 0750620889
- Wang, Z.; Fingas, M.; Page, D. S. (1999) – Oil Spill Identification. Journal of Chromatography A, 843(1-2):369-411. DOI:10.1016/S0021-9673(99)00120-X.